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⑤4硫化亜鉛系薄膜の製造方法

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明　細　書

1．発明の名称

硫化亜鉛系薄膜の製造方法

2．特許請求の範囲

(1) 硫化亜鉛を主成分とし、アルカリ金属、またはアルカリ土類金属の内から少なくとも一種類以上を含有する硫化亜鉛系焼結体をターゲットとし、高周波スパッタリング法により基板上に硫化亜鉛系薄膜を堆積させることを特徴とする硫化亜鉛系薄膜の製造方法。

(2) 前記　硫化亜鉛系焼結体がMn，Cu，Ag，Al，Tb，Dy，Er，Pr，Sm，Ho，Tm，またはこれらのハロゲン化物のうち少なくとも1種類以上を含むことを特徴とする特許請求の範囲第1項に記載の硫化亜鉛系薄膜の製造方法。

(3) 前記アルカリ金属がLi，Na，K，Rb，Csのうち少なくとも1種であることを特徴とする特許請求の範囲第1項記載の硫化亜鉛系薄膜の製造方法。

(4) 前記アルカリ金属の亜鉛に対する濃度が0.1～2原子%であることを特徴とする特許請求の範囲第1項記載の硫化亜鉛系薄膜の製造方法。

(5) 前記アルカリ土類金属がCa，Mg，Sr，Baのうち少なくとも1種であることを特徴とする特許請求の範囲第1項記載の硫化亜鉛系薄膜の製造方法。

(6) 前記アルカリ土類金属の亜鉛に対する濃度が0.02～2原子%であることを特徴とする特許請求の範囲第1項に記載の硫化亜鉛系薄膜の製造方法。

3．発明の詳細な説明

本発明は、硫化亜鉛系薄膜の製造方法に関し、とりわけ、薄膜中に微小粒子や、ピンホールを含まない均質で高品質な硫化亜鉛系薄膜の製造方法に関するものである。

従来、硫化亜鉛系薄膜は、硫化亜鉛系焼結体を電子ビーム蒸着することにより形成されていた。この際用いる硫化亜鉛系焼結体は、硫化亜鉛粉末またはMn，Cu，TbF_3などの活性物質を含む硫化亜鉛粉末を、たとえば400 kg/cm²の圧力で成形

し、不活性ガスまたは硫化水素を含む不活性ガス中で、１０００℃～１２００℃の温度で、１～３時間焼成することにより形成されていた。このように形成した硫化亜鉛系焼結体に電子ビームを照射し、加熱蒸発させ、硫化亜鉛系薄膜を形成した場合、薄膜中に１～２０ミクロンの粒径の微小粒子やピンホールが生ずるという欠点があった。またこのような薄膜をＥＬ薄膜として応用した場合、微小粒子やピンホールが原因となり、絶縁破壊を引き起し、安定なＥＬ素子を形成することができない。

このように薄膜中に微小粒子やピンホールを生ずる原因は、電子ビームを照射した時に硫化亜鉛焼結体が帯電し、静電反発力により微小粒子が飛散し、基板表面に付着するためと考えられる。

一方、硫化亜鉛系薄膜は高周波スパッタリング法によって形成することもできる。すなわち、硫化亜鉛粉末またはＭｎ，ＴｂＦ₃などの活性物質を含む硫化亜鉛粉末を所定の寸法の板に成形し、不活性ガスまたは硫化水素を含む不活性ガス中で１０００～１２００℃の温度で１～３時間焼成することによりターゲットを作成する。ターゲット寸法が大きい場合は上記雰囲気焼成が一般に困難であるので粉末状のまま焼成し、一部焼結した固まりを砕いてターゲットにする場合が多い。

以上の様にして作成したターゲットを用い高周波スパッタリング法で硫化亜鉛系薄膜を作成した場合、電子ビーム蒸着法におけるような微小粒子やピンホールは比較的少ないが、硫化亜鉛自身の化学量論性が悪く、格子欠陥を多くして、特にＥＬ素子に応用した場合、その輝度が低くなる。結局薄膜の結晶性が悪いといえる。

本発明は上記従来技術にもとづき、欠陥のない高品質な硫化亜鉛系薄膜を、特に量産性，低コストに優れているスパッタリング法によって形成する方法を提供するものである。

すなわち、硫化亜鉛を主成分とする粉末に、アルカリ金属またはアルカリ土類金属を添加して、不活性ガスまたは硫化雰囲気中で熱処理することにより形成した硫化亜鉛系焼結体をターゲットにし、高周波スパッタリング法で薄膜形成を行った場合、薄膜中の微小粒子やピンホールが皆無に近く、かつ化学量論性に優れた結晶性の良い高品質で均質な硫化亜鉛系薄膜，特にＥＬ発光において高い輝度を示す薄膜が形成できることを見い出したものである。また従来の焼結体や粉末状ターゲットに比較し、スパッタリングレートが高くなる特徴も見い出された。この原因は、このような方法で作成した硫化亜鉛系焼結体は、密度が高く、粒径が大きいため、ターゲットとした場合、スパッタリングが焼結体表面から均一組成でかつ一様に起るためと考えられる。また添加するアルカリ金属としては、Ｌｉ，Ｎａ，Ｋ，Ｒｂ，Ｃｓ が有効であり、添加量としては、亜鉛に対する濃度が０.１～２原子％が適当であった。

つまり０.１％未満では効果が微弱であり、２％より上では、焼成時に焼成容器と反応する欠点があった。

アルカリ土類金属としては、Ｃａ，Ｍｇ，Ｓｒ，Ｂａが有効であり、添加量としては、亜鉛に対する濃度が０.０２～２原子％が適当であった。つまり、０.０２原子％未満では効果が微弱であり、２原子％より上では、焼成時に焼成容器と反応する欠点があった。また硫化亜鉛系焼結体中に、Ｍｎ，Ｃｕ，Ａｇ，Ａℓ，Ｔｂ，Ｄｙ，Ｅｖ，Ｐｒ，Ｓｍ，Ｈｏ，Ｔｍ，またはこれらのハロゲン化物のうち少なくとも１種類以上を含む場合においても、アルカリ金属またはアルカリ土類金属の添加が有効である。

以下実施例により説明する。市販の硫化亜鉛粉末（粒径０.１～１.５ミクロン）に、種々のアルカリ金属化合物やアルカリ土類金属化合物を添加し、乳鉢により混合した後、約１０重量％の水を加え、さらに混合した後造粒した。この粉末を400kg/cm²の圧力で成形し、直径１５cm，厚さ６mmの円板とし、これを硫化水素雰囲気または不活性ガス雰囲気中で、１０００～１２００℃の温度で、１時間の焼成を行なった。第１表に使用したアルカリ金属化合物またはアルカリ土類金属化合物の種類および濃度，焼成雰囲気，焼成温度，焼成時間，および得られた硫化亜鉛系焼結体の密度（理論密度

に対する割合）を示す。

第　1　表

添加物質		焼成条件			密度
種　類	濃　度（原子%）	雰囲気	温　度（℃）	時　間（hr）	（%）
LiCℓ	2	H_2S	1000	1	91
LiNO	2	H_2S	1000	1	91
NaCℓ	2	H_2S	1000	1	91
KCℓ	2	H_2S	1100	1	90
RbCℓ	2	H_2S	1100	1	90
CsCℓ	2	H_2S	1100	1	90
$BaCℓ_2$	0.3	Ar	1100	1	98
$BaCℓ_2$	0.03	H_2S	1100	1	91
BaCℓ $SrCℓ_2$	0.1 0.1	H_2S	1200	1	98
$BaCℓ_2$ $CaCℓ_2$	0.1 0.1	H_2S	1200	1	98
$BaCℓ_2$ $MgCℓ_2$	0.1 0.1	H_2S	1200	1	98
$Ba(OH)_2$	0.1	H_2S	1100	1	96

第１表から判るように得られた焼結体の密度は、理論密度の９０％以上であった。この焼結体を用いて、高周波スパッタリング法により硫化亜鉛系薄膜を形成したところ、従来の製法の硫化亜鉛系焼結体（一般に理論密度の６５％）や粉末状のターゲットを用いて同様に形成した薄膜に比べて、薄膜中の微小粒子やピンホールがもちろん無く、結晶性の良い高品質な硫化亜鉛系薄膜を形成することができた。

また図面に示すようなＥＬ素子のＥＬ発光体層４を、本発明の方法、すなわち０.０３原子％の塩化バリウムと０.８原子％のＭｎを含む硫化亜鉛系焼結体をターゲットにして高周波スパッタリング法で薄膜を形成し、発光特性（周波数５ＫＨｚの正弦波で励起）を測定した結果、絶縁破壊に対する安定性に優れ、かつ高い輝度のＥＬ素子であることが判明した。

従来法と比較し、その作成条件ならびに特性を第２表にまとめた。

第　2　表

	従来スパッタリング法	本発明スパッタリング法	電子ビーム法
ターゲット	６６％密度 ZnS:Mn	BaCℓ を添加した９１％密度ZnS:Mn	蒸発源 ６５％密度の ZnS:Mn
パワー W/㎠	2.4	2.4	
基板温度℃	２５０	２５０	２２０
アニール温度℃	５５０	５５０	５５０
ガス	Ar	Ar	真空
ガス圧（torr）	3×10^{-2}	3×10^{-2}	5×10^{-6}
スパッターおよび蒸発時間（分）	５	３	３
膜厚 Å	５０００	５０００	５０００
レイト Å/分	１０００	１６６０	１６６０
飽和輝度（フットランバート）	４６０	９５０	９００
安定性	割合絶縁破壊し易い	安定	絶縁破壊し易い
薄膜			微粒子 ピンホールあり

第２表には従来例として電子ビーム法も記してある。この場合、蒸発源として直径１６㎜，厚さ１０㎜の６５％密度の０.８焼結体ペレットを用いた。第２表から明らかなように本発明の高密度のZnS焼結体をターゲットにしてスパッタリング法で作成した薄膜は、従来のスパッタリング法の薄膜に比較し、安定でＥＬ発光強度も約２倍と高い。薄膜作成時のレイトも約１.６倍で効率的である。

また、電子ビーム法に比較しても絶縁破壊の点で優れている。

以上のように、本発明の製法によれば、ピンホールや微小付着物が極めて少なく良質の硫化亜鉛系薄膜が再現性よく形成でき、光学薄膜，蛍光体薄膜，ＥＬ薄膜として応用した場合、光学特性や安定性の優れた素子を形成することができる。

４．図面の簡単な説明

図面は本発明の一実施例の製法方法により形成されたＥＬ素子の構造を示す。

１……ガラス基板、２……透明電極、３……酸化イットリウム薄膜、４……マンガン付活硫化亜

鉛薄膜、5……酸化イットリウム薄膜、6……アルミニウム電極。

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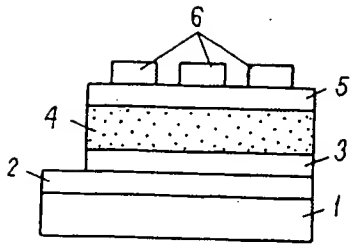

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(54) Manufacturing method of zinc sulfide thin film

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Details
1. Name of invention
Manufacturing method of zinc sulfide thin film

2. Range of the patent claims
(1) It is a manufacturing method of the zinc sulfide related thin film, which shall be characterized by piling the zinc sulfide related thin film on the substrate by the high frequency sputtering method, making zinc sulfide related sintered body as the target, which shall contain the main ingredient as zinc sulfide and at least one kind of the alkaline metals or the alkaline earth metals.
(2) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by containing at least one kind of the halide materials, which are Mn, Cu, Ag, Al, Tb, Dy, Er, Pr, Sm, Ho and Tm as the abovementioned zinc sulfide related sintered body.
(3) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by having at least one kind of Li, Na, K, Rb and Cs as the abovementioned alkaline metals.
(4) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by having the amount of density against the abovementioned alkaline metals to be between 0.1 and 2 atm%.
(5) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by having at least one kind of Ca, Mg, Sr and Ba as the abovementioned alkaline earth metals.
(6) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by having the density against zinc of the abovementioned alkaline earth related metals, which is in between 0.02 and 2 atm%.

3. Detailed explanation of the invention
This invention is concerning the manufacturing method of the zinc sulfide thin film, especially it is concerning the manufacturing method of the high quality zinc sulfide thin film, which does not have small particles nor pin holes within the thin film.

Currently, the zinc sulfide thin film is created by applying the electron beam deposition to the zinc sulfide sintered body. The zinc sulfide sintered body, which is used in this case, is created by firing for one to three hours at the temperature of between 1000 °C and 1200 °C within the inert gas or the inert gas which shall contain hydrogen sulfide after

molding zinc sulfide powder or zinc sulfide powder which shall contain the active substance such as Mn, Cu or TbF_3, etc. at the pressure of 400 kg / cm^2. In the case that the zinc sulfide thin film is created by the zinc sulfide sintered body, which the electron beam is irradiated to and shall be evaporated by heating, there was a problem of generating small particles of the particle sizes of 1 to 20 micron and pin holes within the thin films. Also, when applying such thin films for the purpose of the EL thin film, because of the small particles and pin holes, insulation destruction shall occur, and as a result, it is not possible to create a stable EL element.

The cause of generating small particles and pin holes is because the zinc sulfide sintered body is charged when the electron beam is irradiated, and small particles are scattered by the electrostatic repulsion, then they would be stuck to the surface of the substrate.

On the other hand, the zinc sulfide thin film can also be created by the high frequency sputtering method. Therefore, the target shall be created by firing for 1 to 3 hours at the temperature of between 1000 and 1200 °C within the inert gas or the inert gas which shall contain hydrogen sulfide after molding the zinc sulfide powder or the zinc sulfide powder which shall contain the active substance such as Mn, Cu or TbF_3, etc., into the board with the designated measurement. In the case that the target measurement is large, because the abovementioned atmosphere firing would become generally difficult, firing would most likely be made with the powder condition, then the target would be made by smashing the lump, which is partly sintered. In the case that zinc sulfide thin film is made by the high frequency sputtering method using the target, which is created as mentioned, there are relatively smaller numbers of small particles and pin holes as it occurs when the electron beam deposition is applied, however, stoichiometry of the zinc sulfide is bad, which shall create more lattice defects, and especially when it is applied for the EL element, the luminance shall become low. After all, it means that the crystallization of this thin film is bad.

This invention is made to provide the forming method based on the abovementioned existing technique, in order to create high quality zinc sulfide thin film without any defects using the sputtering method, which is excellent for mass production and excellent in the cost performance.

When the thin film forming is applied by the high frequency sputtering method making the target as zinc sulfide sintered body, which is created by giving the heat treatment within the inert gas atmosphere or sulfide atmosphere to the powder, which shall have the main ingredient as zinc sulfide, which either alkaline metals or alkaline earth metals is added to, it was found out that such thin film can be created, which shall indicate high luminance, especially at EL emitting, and shall show almost no small particles nor pin holes within the thin film, and shall have high quality and even zinc sulfide thin film with excellent stoichiometry and crystallization. Also, compared to the existing sintered body and powder style target, it was found out that the sputtering rate became higher. It is probably because when creating the zinc sulfide sintered body using such a method, the density would be high and the particle size would be large, therefore, by making it as the target, sputtering shall occur from the surface of the sintered body at the even

composition and equally to the whole surface. Also, as for the adding alkaline metals, Li, Na, K, Rb or Cs are effective, and as to the addition amount, 0.1 atom% to 2 atom% of the thickness against zinc was the suitable amount. Therefore, if it is less than 0.1%, the effect would be very weak, and if it is more than 2%, it would react against the firing container when firing.

As for the alkaline earth metals, Ca, Mg, Sr and Ba are effective, and as for the additional amount, 0.02 atom% to 2 atom% of the thickness against zinc was the suitable amount. Therefore, if it is less than 0.02 atom%, the effect would be very weak, and if it is more than 2 atom%, it would react against the firing container when firing. Also, in the case that at least one of the halide of Mn, Cu, Ag, Al, Tb, Dy, Ev, Pr, Sm, Ho or Tm is contained, the addition of the alkaline metal or the alkaline earth metal would also be effective.

Hereinbelow, an explanation shall be made according to the implementation example. Various alkaline metallic compounds or various alkaline earth metallic compounds are added to the zinc sulfide powder (particle size 0.1 to 1.5 micron, goods on the market), and after mixing shall be performed by a mortar, approximately 10 weight% of water shall be added, and mixed together again, then granulated. This powder was molded at the pressure of 400 kg/cm^2 in order to create a circle board of the diameter 15cm and the thickness 5mm, then firing was performed to this within the inert gas atmosphere at the temperature of between 1000 and 1200 °C for one hour. Table 1 shall indicate the type, firing atmosphere, firing temperature and firing period of the alkaline metallic compound or the alkaline earth metallic compound used as well as the density of the zinc sulfide sintered body, which was obtained (rate against theoretical density).

Table 1 (P.195, left upper)

Addition substance		Firing condition			Density (%)
Type	Thickness (atom%)	Atmosphere	Temperature (°C)	Time (hour)	
LiCl	2	H_2S	1000	1	91
LiNO	2	H_2S	1000	1	91
NaCl	2	H_2S	1000	1	91
K Cl	2	H_2S	1100	1	90
RbCl	2	H_2S	1100	1	90
CsCl	2	H_2S	1100	1	90
$BaCl_2$	0.3	Ar	1100	1	98
$BaCl_2$	0.03	H_2S	1100	1	91
BaCl $SrCl_2$	0.1 0.1	H_2S	1200	1	98
$BaCl_2$ $CaCl_2$	0.1 0.1	H_2S	1200	1	98
$BaCl_2$ $MgCl_2$	0.1 0.1	H_2S	1200	1	98
$Ba(OH)_2$	0.1	H_2S	1100	1	95

As it is seen from Table 1, the density of the sintered body, which is obtained, was more than 90% of the theoretical density. Using this sintered body, zinc sulfide thin film was created by the high frequency sputtering method. The result was that it was able to create the zinc sulfide thin film of higher quality and good crystallization compared to the thin film, which is created using the target of the zinc sulfide sintered body (generally 65% of the theoretical density) and powder style, which are made by the existing manufacturing method, and it had no small particles and pin holes within the thin film.

The thin film was created by the manufacturing method of this invention, which shall mean that the thin film was created by using the high frequency sputtering method making the target as the zinc sulfide sintered body, which shall contain Mn of 0.8 atom% and barium chloride of 0.03 atom%, as for the EL emission layer 4 of the EL element, which is shown in the figure, and then the emitting characteristic (excitation occurs at the sine wave of the frequency 5 KHz) was measured. As a result, it was found that the EL element was stable against the insulation destruction as well as having the high luminance.

Table 2 shows the creating condition and the characteristics compare to the existing method.

Table 2 (P.195, left, bottom)

	Existing sputtering method	Sputtering method of this invention	Electron beam deposition method
Target	ZnS : Mn of 65% density	ZnS : Mn of 91% density, BaCl is added	Evaporation source ZnS : Mn of 65% density
Power W / cm^2	2.4	2.4	
Substrate temperature °C	250	250	220
Anneal temperature °C	550	550	550
Gas	Ar	Ar	Vacuum
Gas pressure (torr)	3×10^{-2}	3×10^{-2}	5×10^{-6}
Sputtering and evaporation time (min.)	5	3	3
Film thickness Å	5000	5000	5000
Rate Å / min.	1000	1660	1660

Saturated luminance (Foot Lambert)	450	950	900
Stability	Relatively easy to have insulation destruction	Stable	Easy to have insulation destruction
Thin film			Small particles and pin holes exist

Table 2 indicates the results of the electron beam deposition method as an example of the existing methods. In this case, the 0.8 sintered body pellet of 65% density, thickness of 10 mm and the diameter of 15 mm was used for the evaporation source. As it is clearly seen from Table 2, the thin film, which is created by the sputtering method making the target as the ZnS sintered body of high density of this invention, is stable and the emitting intensity is approximately twice as much compared to the thin film, which is created by the existing sputtering method. The rate when creating the thin film is also approximately 1.6 times, which is efficient.

Also, it is better compared to the electron beam deposition method from the insulation destruction point.

As it is mentioned, by using the manufacturing method of this invention, high quality zinc sulfide thin film, which produces extremely small numbers of pin holes and small particles, can be created with a good reproduction, and when it is applied to the use of the optical thin film, the phosphor thin film and the EL thin film, it is able to create the element with excellent stability and optical characteristics.

4. Simple explanation of the figure

The figure shows the structure of the EL element, which is created by the manufacturing method of the implementation example of this invention.

1. Glass substrate
2. Transparent electrode
3. Yttrium oxide thin film
4. Manganese added zinc sulfide thin film
5. Yttrium oxide thin film
6. Aluminum electrode

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